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AMINE VULCANIZATION OF ETHYL POLYACRYLATE

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Early attempts to vulcanize saturated acrylic resins are attributed to Röhm (5) and later to Novak (4). According to present-day understanding of the properties of these polymers, it is unlikely that either investigator succeeded in obtaining a true vulcanizate.

Mast and Fisher investigated amine curing agents in connection with a study of the curing characteristics of halogen-containing copolymers of ethyl acrylate (2). In the course of this work, they attempted to cure ethyl polyacrylate with triethylene tetramine. The results suggested that, at best, a low-grade cure had been obtained (3). The inference was that the halogen-containing co-monomer was necessary for the successful vulcanization of the ethyl acrylate copolymers.

Recently, experiments conducted in this Laboratory have demonstrated that under the proper conditions certain nitrogen-containing compounds can be used to vulcanize the n-alkyl polyacrylates. The purpose of presenting these preliminary findings is to announce this new development in the field of acrylic rubbers.

EXPERIMENTAL

The scorch test (6,7) which employs a Mooney Viscometer,¹ was used in these experiments to examine the effect of various compounding ingredients on the rate of cure of acrylic polymers. The study of ethyl polyacrylate was emphasized because of the potential value of this material in the field of heat-resistant rubbers. In general, the polymer was mixed with SRF black and stearic acid as a master batch in a Banbury Mixer. Other ingredients were added on a 6-by 12-inch laboratory mill, and the milling was continued according to recommendations in American Society for Testing Materials D 15-41. The stock was then refined and removed from the mill at a finished thickness of about one eighth inch. Disks of the size required for the Mooney Viscometer were cut from the compounded sheet with the aid of a die. Usually about six disks totaling 35 grams, were required to fill the cavity.²

The disks were placed in the viscometer, which was controlled at 300° + 3° F., and preheated for 1-minute; then the rotor was set in motion. Dial readings were taken every minute for 30 minutes. Any tendency for the test stock to cure was recognizable as an increase in the viscosity 6 to 12 minutes after the test had begun.

¹ THE MENTION OF COMMERCIAL PRODUCTS DOES NOT IMPLY THAT THEY ARE ENDORSED OR RECOMMENDED BY THE DEPARTMENT OF AGRICULTURE OVER OTHERS OF A SIMILAR NATURE NOT MENTIONED.

² ALTHOUGH THE LAMINATING OF SPECIMENS IN THIS MANNER IS NOT NORMALLY RECOMMENDED BECAUSE OF THE POSSIBILITY OF AIR INCLUSIONS, NO SPURIOUS EFFECTS WERE ENCOUNTERED WHICH COULD BE ATTRIBUTED TO FAULTY TECHNIQUE. NUMEROUS SPECIMENS OF ACRYLIC POLYMERS MADE IN THIS WAY HAVE BEEN EXAMINED, BUT NONE HAS SHOWN SIGNS OF PITTING OR BLOWING.

The tensile properties of the various vulcanizates were determined by the usual ASTM procedure, D 412-41, in which dumbbells stamped from slabs that had been cured at 298° F. in standard molds (ASTM, D 15-41) were used.

Swelling measurements were determined on 1- by 1-1/2-inch rectangles cut from the same sheet as the tensile dumbbells. Since the swelling of vulcanized ethyl polyacrylate in water at room temperature is a rather slow process, all the specimens discussed in this circular were swollen in boiling water. The shape of the volume swelling versus time curve is of such type that swelling at 48 hours can be used to indicate equilibrium swelling without introducing a serious error.

Preliminary heat aging of the vulcanizates can be reported for some of the recipes studied. Test data were obtained on standard dumbbells which had been hung in a mechanical convection oven at 300° F. for various lengths of time.

RESULTS AND DISCUSSION

Table 1 shows the various recipes used to demonstrate that triethylene tetramine in the proper formulation can yield a vulcanizate with useful properties. Unless otherwise mentioned, the temperature of the milling rolls during the incorporation of the amines was maintained at 150° ± 2° F. In recipe A, Trimene Base (triethyl trimethylene triamine) and stearic acid were compounded with ethyl polyacrylate. This amine can cure the polymer Lactoprene EV (95% ethyl acrylate - 5% β -chloroethyl vinyl ether) to a satisfactory vulcanizate. Under the conditions of test in this study, however, there was no tendency for the Trimene Base to cure ethyl polyacrylate, as demonstrated by the scorch test data. On the other hand, under the same experimental conditions, a sample containing triethylene tetramine (recipe D) instead of Trimene Base showed a strong inclination to cure. An ethyl polyacrylate control stock containing stearic acid (recipe B) showed no appreciable tendency to vulcanize and similarly another stock containing only the two parts of triethylene tetramine (recipe C) cured extremely slowly, if at all. Evidently the presence of stearic acid is essential not only as an aid in the incorporation of the black but also as an accelerator for the curing process.

The milling temperature was also important in obtaining a satisfactory vulcanizate in a reasonable length of time, although no attempt was made to determine the optimum temperature or temperature range which would yield a well-cured sample. A stock containing two parts of triethylene tetramine (recipe E), milled on cold rolls (50° F.) showed signs of delayed curing whereas a similar stock (recipe F) milled on hot rolls (200° F.) cured rapidly. This activation seems to persist, because it was demonstrated that a sample compounded on hot rolls still exhibited the same curing characteristics after storage for 24 hours at room temperature.

The scorch test data of recipes G and H indicate that a somewhat higher rate of cure is obtained by adjusting the proportions of stearic acid and triethylene tetramine. A few experiments were attempted in which the recipe was further modified by the addition of common vulcanizing agents and accelerators. The only one of particular interest here was a sample containing two parts of triethylene tetramine and two parts of sulfur (recipe I). It is evident that sulfur tends to act as an inhibitor for the cross linking reaction. This effect seems to be characteristic of the vulcanization of ethyl polyacrylate with triethylene tetramine, since in curing Lactoprene EV with triethylene tetramine and sulfur, this inhibition of initial cure has never been noticed. Another significant observation is that in the vulcanization of Lactoprene EV with Trimene Base (triethyl trimethylene triamine), stearic acid does not appear to accelerate the curing rate. This is contrary to the observations on ethyl polyacrylate discussed above.

No attempt has been made to test all the possible amines. It seems reasonably safe to say at this time, however, that aromatic amines such as diphenyl guanidine, Accelerator 808, Tonox, and the three phenylene diamines do not exhibit any disposition to cure ethyl polyacrylate under the conditions employed in this study. All the amines of the homologous series diethylene triamine to pentaethylene hexamine strongly display this inclination to vulcanize ethyl polyacrylate. These compounds cure the polymer at about the same rate, although the diethylene triamine appears to be slightly more active. The only test completed with these amines is the scorch test, so that no information is available about the physical properties of the cured stock. It is, however, believed that the tensile properties and water resistance would approximate those obtained for a vulcanizate cured with triethylene tetramine.

The physical properties of the vulcanizates suggest that this material may have useful properties. Some of the properties of several vulcanizates made according to slightly varying recipes are presented in Table 2. All these samples were cured at 298° F. for 60 minutes, and some variation in the extent of cure is probable. Nevertheless, it is significant that the vulcanizates from the three recipes illustrated yield stocks with useful tensile properties and that the swelling in boiling water for 48 hours is not particularly excessive. The SRF black in the recipes could be replaced with an HMF black, for example, with a probable improvement in water resistance. Ethyl polyacrylate stocks compounded on recipes similar to those in Table 1 and cured for 120 minutes at 298° F. have swelled as little as 13 percent in boiling water. The simple recipes employed thus far do not yield samples with heat resistance comparable with that of vulcanizates described in a paper on Lactoprene EV (1). Since it has been reported that the heat resistance of the acrylic copolymer is definitely dependent on the recipe (1), it is believed that an amine recipe will be found which will give improved heat resistance to ethyl polyacrylate. The resistance to dry heat reported here is still far superior to that of natural rubber and better than that of most synthetic rubbers.

TABLE I

Comparative data demonstrating the effect of vulcanizing agent, stearic acid, and milling temperature on the curing characteristics of ethyl polyacrylate.

Ingredients, parts by weight	Recipes									
	A	B	C	D	E	F	G	H	I	
Ethyl polyacrylate	100	100	100	100	100	100	100	100	100	
Stearic Acid	1	1	-	1	1	1	1	3	1	
Triethyl trimethylene triamine (Trimene Base)	2	-	-	-	-	-	-	-	-	
Triethylene tetramine	-	-	2	2	2	2	3	2	2	
Sulfur	-	-	-	-	-	-	-	-	-	
SRF black	70	70	70	70	70	70	70	70	70	
Milling temperature, ° F.	150	150	150	150	50	200	150	150	150	
Curing characteristics at 300° F.										
Scorch point (T _s), min. ¹	> 20	> 20	13	4	6	4	3	3	8	
Viscosity at T _s (V _m) ²	21.8	37.0	29.9	27.9	10.0	33.2	35.1	32.1	32.1	
Cure point (T _c), min. ³	no	no	> 30	17.3	29.5	15.6	15.7	12.9	> 30	

¹ Time required to reach the lowest viscosity reading which precedes a consistent rise.

² Viscosity at the scorch point.

³ Time required to reach a point having a viscosity of 30 units above the minimum.

TABLE 2

Physical properties of experimental ethyl polyacrylate vulcanizates

	<u>Recipes</u>		
	A	B	C
Ethyl polyacrylate, part	100	100	100
Stearic acid, part	1	3	3
Triethylene tetramine, part	2	1	2
SRF black, part	50	50	50
Curing time at 209° F., min.	60	60	60
<u>Properties</u>			
Tensile strength, p.s.i.	1540	1490	1500
Ultimate elongation, percent	590	790	530
Modulus at 200%, p.s.i.	340	220	420
Durometer hardness, 30 sec.	38	39	45
Brittle point, °C.	-15	-15	-15
Volume increase in 48 hours in water at 212° F., percent	21	21	17
<u>Properties after aging for 3 days at 300° F.</u>			
Tensile strength, p.s.i.	1130	830	1210
Ultimate elongation, percent	180	480	180
Modulus at 200%, p.s.i.	-	280	-
Durometer hardness, 30 sec.	56	49	60

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